

Synthesis of lead oxide nanoparticles by Sonochemical method and its application as cathode and anode of lead-acid batteries

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Abstract

This paper discusses the results of a research aimed at investigating the synthesis of nanostructured lead oxide through reaction of lead nitrate solution and sodium hydroxide solution in the presence of constant frequency ultrasonic waves (Sonochemical method) and polyvinyl pyrrolidone (PVP) as structure director. At first, lead hydroxide was obtained in a synthesized solution and then, after filtration, it was dehydrated at the temperature of 320 °C so that nanostructured lead oxide can be produced. The effects of different parameters including lead nitrate concentration, sodium hydroxide concentration, synthesis temperature, treatment time and PVP concentration were optimized by a “one at a time” method. The prepared lead oxide powder was characterized by scanning electron microscopy (SEM), transmission electron spectroscopy (TEM) and X-ray diffraction (XRD). Under optimum conditions, uniformed and homogeneous nanostructured lead oxide powder with more spongy morphology and particle size of 20–40 nm was obtained. The synthesized lead oxide, as anode and cathode of lead-acid batteries, showed very excellent discharge capacity (230 mA h g^{−1}) and cycle life.

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1. Introduction

Our goal in this research was to obtain an easy method to synthesize more porous and spongy nanostructured lead oxide. Such a structure probably can be useful in pigments and active materials of lead-acid batteries. During the last few years, synthesis of nanostructured oxide materials has attracted considerable attention [1–5].

Nowadays, the awakening of public concern over the environmental problems caused by gasoline-fueled vehicles, especially in large cities, has led to worldwide interest for the development of efficient electrical and hybrid vehicles. Battery, as an autonomous energy system, is a key element in the operation of the electrical vehicles due to its great influence on the final cost, range and performance of the vehicle. Characteristics of the batteries available in the market today impose heavy restrictions to the performance of the electrical vehicles.

Lead-acid batteries developed as widespread articles of commerce in over a century. The concept of lead-acid batteries came into existence with the research and inventions of Raymond Gaston Planté in 1860, although batteries containing sulfuric acid or lead components were discussed earlier [6]. Some advantages of lead-acid batteries include: low cost of manufacture, simplicity of design, reliability and relative safety when compared to other electrochemical systems. Relatively good specific power has caused widespread use of lead-acid batteries in starting, lighting and ignition of engine (SLI) purposes for vehicular (e.g., automotive, marine and aviation) applications. The lead-acid system has also found widespread use in traction batteries in gulf carts and boats. However, the use of lead-acid batteries for electric cars as an alternative to fossil fuels has been limited by the need for better specific energy and deep discharge cycle life.

Because of the above-mentioned advantages of lead-acid batteries, there is a big interest to improve and develop lead oxide characteristics so that more discharge capacity and more cycle life can be obtained. Many researches are conducted to improve discharge capacity of lead oxide and lead dioxide [7–15]. In recent years, there has been an increase in the amount of trends

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focusing on nanotechnological methods to prepare nanoparticle with extended advantages.

The lead element has many oxide forms including PbO (α , β and amorphous), Pb₂O₃, Pb₃O₄, PbO₂ (α , β and amorphous). Among lead oxides, lead dioxide (PbO₂) has been studied more than any other forms. A number of electrochemical techniques have been used to prepare lead dioxide some of which are constant current and constant potential [16], cyclic voltammetry [17] and pulse current methods [18]. Shen and Wei [16] deposited lead dioxide from a solution containing Pb²⁺ on three different substrates (i.e. Au, Pt and Ti) with different techniques.

We previously reported a new method for electrochemical synthesis of nanostructured PbO₂ [19] and used the obtained PbO₂ as cathode of rechargeable lead-acid batteries [20]. Nevertheless, there are only few reports on the synthesis of lead oxide in nano-scale. Cruz et al. showed that the spray pyrolysis method can be used for synthesis of lead oxide from lead salt solution; however, they did not focused on preparing nanostructures. They synthesized just a lead oxide thin film by spray pyrolysis of lead salt solution on a preheated surface [21]. Konstantinov et al. used the spray pyrolysis method for synthesis of nanostructured lead oxide. They had a systematic study of the effect of various spray pyrolysis parameters such as temperature, solution concentration and solution flow rate on the morphology, crystallization process, crystal size and specific surface area. They synthesized globular shape lead oxide in the wide range of particle size of 20–127 nm [22].

There are many reports on the effect of ultrasonic waves on morphology and particle size in synthesized solutions. In many reports, the ultrasonic-affected synthesized solution is called Sonochemical solution while the method used for synthesis being called “Sonochemical method” [23–30]. The ultrasonic affect on synthesized system in many ways is strongly dependent on system species and reaction mechanism. Zhang et al. have reported that the Sonochemical method is an effective way of stabilizing the nanometer-sized particles produced during synthesis processes [31]. The first and simplest effect of ultrasonic waves on synthesized solutions is preventing the particle growth and breaking agglomerated and colonial balks into small particles.

In this method, we tried to use a technique introducing a new easy method for preparing homogeneous porous nanostructured lead oxide. In this manner, fixed frequency ultrasonic waves were used as a useful tool to prevent growth and help formation of nanoparticles; moreover, polyvinyl pyrrolidone (PVP) was used as a structure director additive.

2. Experimental

2.1. Materials

Analytical grade Pb(NO₃) (Loba Chem, India), NaOH (Loba Chem, India), polyvinyl pyrrolidone (Loba Chem, India), sodium dodecyl sulfate (Fluka), sodium dodecyl benzene sulfonate (Aldrich) and cetyl trimethyl ammonium bromide (Merck) were used without any purification. Ethanol (Bidestan Co., Iran) was distilled before being used. Sulfuric acid, lead nitrate and glycerol were produced by Loba Chem Co. (India). Palladium(II) chloride was obtained from Merck. Rashel salt, tin chloride, hydrochloric acid, copper sulfate and carbon black were produced by Iranian companies in industrial grade. Doped polyethy-

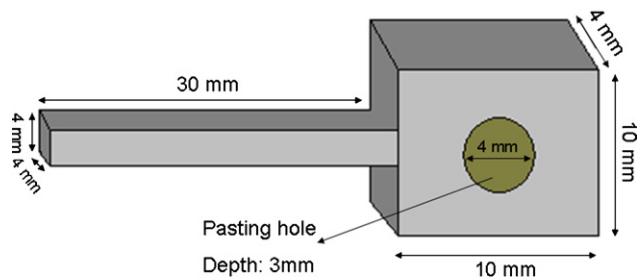


Fig. 1. Scheme and dimensions of the used electrode.

lene was obtained from Zipperling Co. Humic acid (3,4,5-trihydroxybenzoic acid), 1,2-acid (α -hydroxy- β -naphthalene carboxylic acid) and barium sulfate at industrial grade were used as additive to negative paste. In all experiments, distilled water was used. The calcium–tin–lead alloy was used for electrode making. The structure of used electrode is shown in Fig. 1.

2.2. Instruments

The characterization of sample powders was performed through scanning electron microscopy (SEM; SEM studies were performed using a Philips XL30 Model). Titration system was placed on bath vessel of ultrasonic instrument. Ultrasonic bath (Tecna6) made by Tecno-Gaz Co. (Italy) was used for sonicating of solutions. Transmission electron microscopy (TEM) and X-ray diffraction (XRD) along with TEM investigations were performed using a Ziess EM900. Powder samples were analyzed by an XRD instrument made by Philips Co. (X Per), using the Cu K α radiation and graphite monochromator.

2.3. Procedure

2.3.1. Synthesis procedure

All experiments were performed under atmosphere conditions. A lead nitrate solution (0.02 M) including structure director additive (10 g l⁻¹) was sonicated for 30 min and then, enough volume of sodium hydroxide solution was slowly added (similar to titration method). In this step, nanostructured lead hydroxide was formed during the following reaction (1):



At the end of the process of adding sodium hydroxide solution, the mixture was additionally sonicated for 30 min. The precipitated lead hydroxide was filtered and washed with distilled water and ethanol for three times. The obtained precipitation was introduced into 50 mL of ethanol and the mixture was sonicated for 30 min and then, the sonicated mixture was filtered. The final obtained precipitation was dehydrated at 320 °C for 3 h. The following reaction (2) happened during the dehydration phase:



Table 1

The conventional formulation of negative paste for the used batteries

No.	Compound	wt%
1	Lead oxide nanopowder	99.27
2	Carbon black	0.15
3	CMC	0.1
4	Humic acid	0.1
5	1,2-Acid	0.1
6	Barium sulfate	0.2
7	Polyacrylamide fiber	0.08

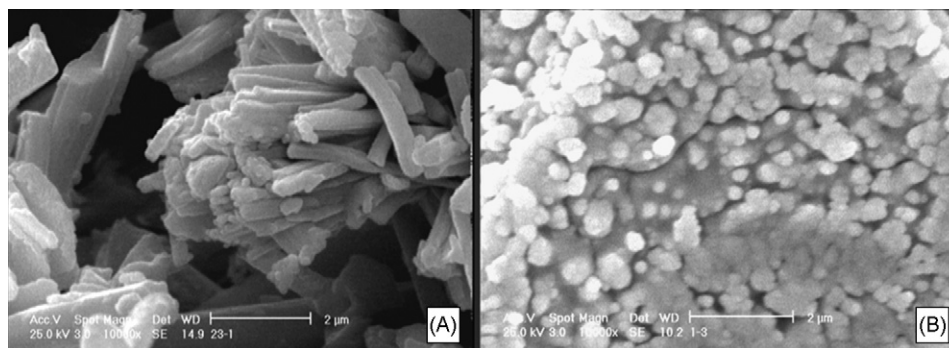


Fig. 2. SEM images of samples which synthesized in the absence (A) and in the presence (B) of ultrasonic waves. Other conditions were constant as following: synthesis temperature 40 °C, 0.1 M lead nitrate, 0.2 M sodium hydroxide and 0.0 M PVP.

At dehydration phase, nanostructured lead oxide was formed. The nanoparticles were sonicated in ethanol for 30 min to eliminate agglomeration. At final step, the mixture was filtered and dried at 110 °C. The final product was obtained in powder form. The nanostructured lead oxide powder was characterized by SEM, TEM and XRD.

2.3.2. Battery production and test

Negative paste was prepared conventionally with the formulation shown in Table 1. Required amounts of lead oxide nanopowder, carbon black, barium sulfate, 1,2-acid, humic acid and polyacrylamide fibers were mixed together in a small paste mixer for 15 min. 0.5 ml water (per 1 g lead oxide) was added to above mixture and mixed for 5 min. Then, 1 ml sulfuric acid (1.25 g cm^{-3}) was gradually added. Paste was mixed for a period of time so that it becomes suitable for pasting. Paste temperature was kept lower than 60 °C. The prepared negative paste was pasted on the pasting hole of electrode (a one-hole plate, see Fig. 1).

Positive paste was prepared conventionally and the process of preparation was exactly similar to that of negative paste. It should be mentioned that in positive paste some additives including carbon black, barium sulfate, 1,2-acid and humic acid were not used. The positive electrode (the one-hole plate) was the same as negative electrode.

The pasted negative and positive electrodes were cured in a small laboratory home-made curing vessel at relative humidity of 95% and temperature of 70 °C. The cured pasted electrodes were dried at 80 °C for 6 h. Each dried negative pasted electrode was coupled with a commercial positive plate (a product of Aranniru Company, Iran) and also each dried positive pasted electrode was coupled with a commercial negative plate (a product of Aranniru Company, Iran) so that testing batteries could be made. The electrochemical formation process of the constructed batteries was performed at sulfuric acid solution with density of 1.24 g cm^{-3} using constant voltage method (2.48 V per cell) for 48 h.

3. Results and discussion

3.1. Ultrasonication effect

Our studies showed that, in this method, ultrasonic wave was one of the effective factors involved in synthesizing uniform nanostructured lead oxide. There are some other effective parameters in the suggested method including concentration of lead nitrate, sodium hydroxide and additives and synthesis temperature. The effect of all parameters was optimized by “one at a time” method [32]. In all optimization experiments, the volume of 100 ml was used for lead nitrate and sodium hydroxide solutions; subsequently the final volume was 200 ml.

What effects do ultrasonic waves have on particle size and morphology of lead oxide? This was the first question; two synthesis processes were carried out at the same conditions of temperature (40 °C) and concentrations (0.1 M lead nitrate,

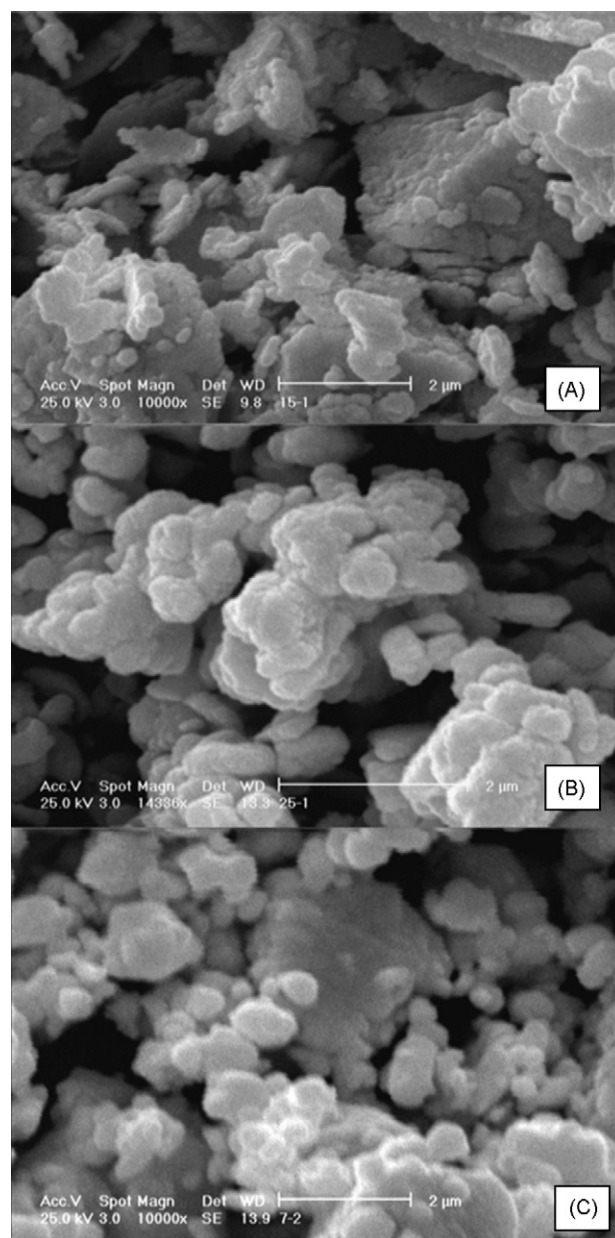


Fig. 3. SEM images of three samples of lead oxide synthesized at lead nitrate concentrations of 0.05 M (A), 0.2 M (B) and 0.02 M (C). Other conditions were constant as follows: synthesis temperature of 40 °C, 0.2 M sodium hydroxide and in the absence of PVP.

0.2 M sodium hydroxide) in the presence and absence of ultrasonic waves without any structure director additives. Fig. 2 shows the SEM images of lead oxide powders which are synthesized in the presence and absence of ultrasonication. As it is seen from Fig. 2, the presence of ultrasonic waves makes lead oxide particles more uniform and smaller.

3.2. Concentration optimization of reagents

After confirming of positive effect of ultrasonication, the concentration of lead nitrate solution was varied from 0.005 to 0.2 M at temperature of 40 °C and sodium hydroxide concentration of

0.2 M. Morphology and particle size of each sample were studied by SEM. SEM results showed that lead nitrate concentration of 0.02 M produces more uniform and smaller particles. SEM images of three samples used in these experiments are shown in Fig. 3. As it is evident in Fig. 3C, 0.02 M lead ion (Pb^{2+}) produces smaller particles. The conclusion is that at lower concentrations of lead ions, the rate of particle growth is less than the rate of nucleation; while at higher concentrations, growth and agglomeration and other mechanisms involved in the formation of heavy particles are more manifest. At concentrations lower than 0.02 M, no considerable change in morphology and particle size is observed. On the other hand, at lower concentrations, the amount of synthesized lead oxide is low and as a result, filtra-

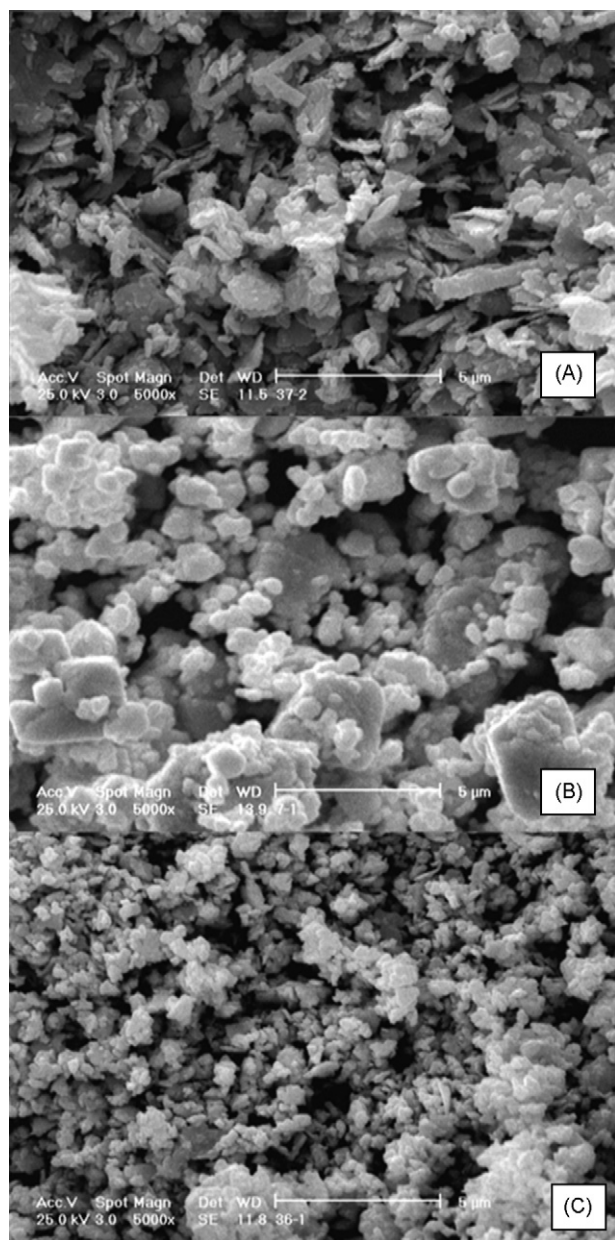


Fig. 4. SEM images of three samples of lead oxide synthesized at sodium hydroxide concentrations of 0.01 M (A), 0.4 M (B) and 0.04 M (C). Other conditions were constant as follows: synthesis temperature of 40 °C, 0.02 M lead nitrate and in the absence of PVP.

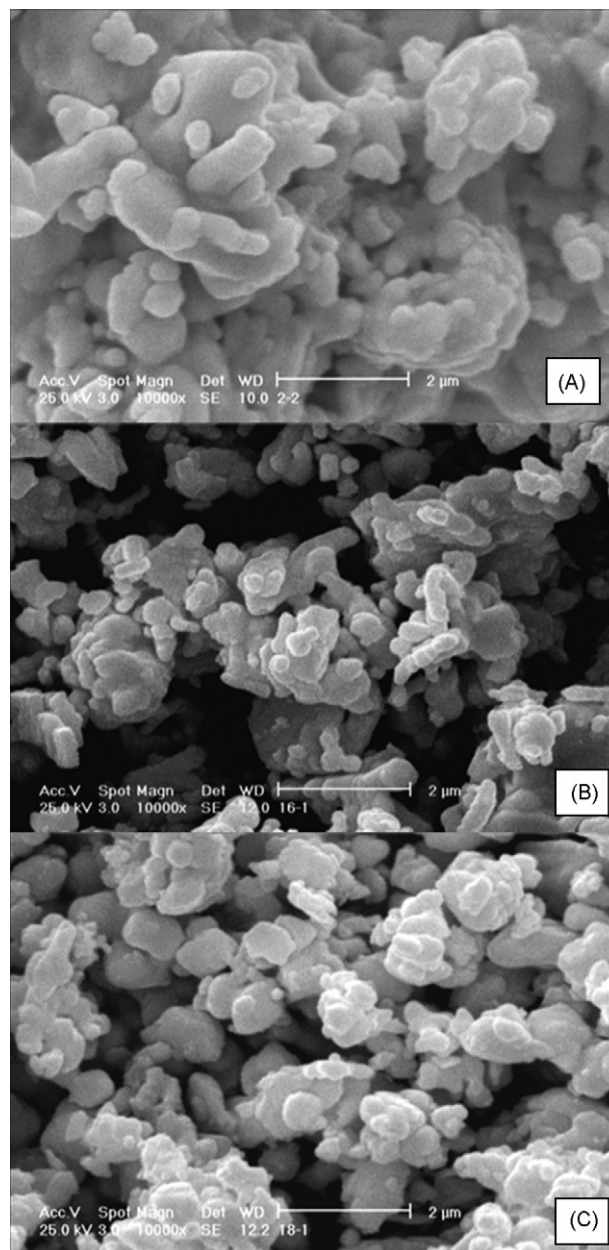


Fig. 5. SEM images of three samples of lead oxide synthesized at temperature of 0 °C (A), 70 °C (B) and 40 °C (C). Other conditions were constant as follows: 0.02 M lead nitrate, 0.04 M sodium hydroxide and 0 M PVP.

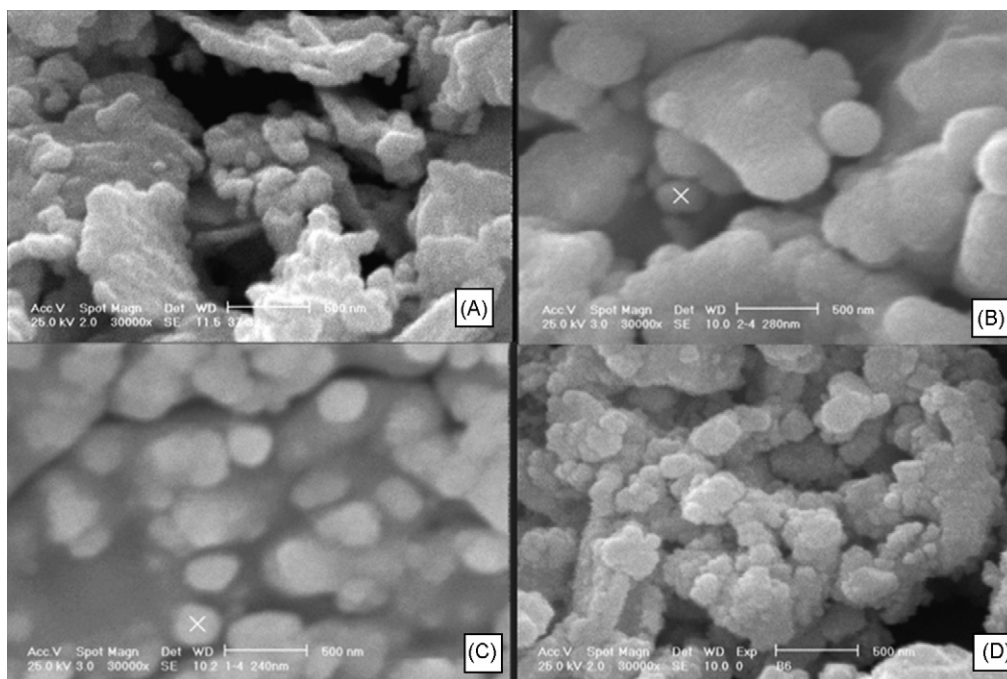


Fig. 6. SEM images of four samples of lead oxide synthesized in the presence of different structure director additives with concentration of 6 g l^{-1} : sodium dodecyl sulfate (A), sodium dodecyl benzene sulfonate (B), cetyl trimethyl ammonium bromide (C) and polyvinyl pyrrolidone (D). Other conditions were constant as follows: temperatures of 40°C , 0.02 M lead nitrate and 0.04 M sodium hydroxide.

tion and other processes happen with more difficulty. Therefore, the concentration of 0.02 M for lead nitrate was selected as the optimum concentration.

At the optimum concentration of lead ions (0.02 M), sodium hydroxide concentration was varied from 0.01 to 0.4 M . The effect of hydroxide ions concentration on particle size and morphology was investigated by SEM. The SEM images of the synthesized samples showed that at hydroxide concentration of 0.04 M , smaller and uniform particles of lead oxide can be produced. As an example, three SEM images for three different concentrations of hydroxide are shown in Fig. 4. As it is seen from Fig. 4, at lower concentrations of sodium hydroxide, lead oxide particles are non-uniform while at higher concentrations the final particles are bigger and more agglomerated.

3.3. Temperature effect

Six synthesis processes were made at 0 , 20 , 40 , 70 , 80 and 90°C so that the effect of synthesis temperature on morphology and particle size of lead oxide powder can be investigated. Fig. 5 shows the effect of temperature on morphology and particle size of nanostructured lead oxide. The SEM images of synthesized powders showed that at 40°C , smaller and more uniform particles are produced probably because of the fact that at this temperature, growth rate, nucleation rate and agglomeration rate are suitable for formation of optimum powder.

3.4. Structure directors

There are some reports on the positive effects of a few compounds, used as synthesis additives, on the formation of

suitable products. For example, Cao et al. reported that cetyl trimethyl ammonium bromide (CTAB) can be used as a useful additive for the synthesis of PbO_2 and Pb_3O_4 [33]. They reported that CTAB played an important role in determining the morphology of products. According to their report, nanorod growth is due to specific interactions between the cationic surfactant (CTAB) and anionic specie of $\text{Pb}(\text{OH})_3^-$. We studied the effect of four different additives on morphology and particle size of lead oxide powder. Fig. 6 shows the effect of four various structure director additives on morphology of lead oxide. As it is evident in Fig. 6, sodium dodecyl sulfate (SDS), sodium dodecyl benzene sulfonate (SDBS) and CTAB are not suitable to obtain uniform nanostructure. Fig. 6D shows that PVP, as a structure director, organizes uniformly the nanostructure of lead oxide in smaller sizes therefore; PVP was selected as a suitable additive for synthesizing of lead oxide.

Finally, PVP concentration in synthesis solution was varied from 1 to 50 g l^{-1} to optimize the concentration of PVP and to obtain the best structure for the final product (PbO) during 6 synthesis processes in 6 different concentrations of PVP. Fig. 7 shows the SEM images of lead oxide obtained in the presence of three different PVP concentrations. As it is shown in Fig. 7, at PVP concentration of about 20 g l^{-1} , lead oxide structure is very different from the others. At this concentration, lead oxide can be synthesized in excellent and more porous nanostructure (moss shape). Lead oxide in optimum nanostructures can be very useful in different applications such as energy storage devices, pigments, etc.

Zhang et al. [34] reported that PVP probably organizes the nanostructures by forming a cation–PVP complex (Scheme 1).

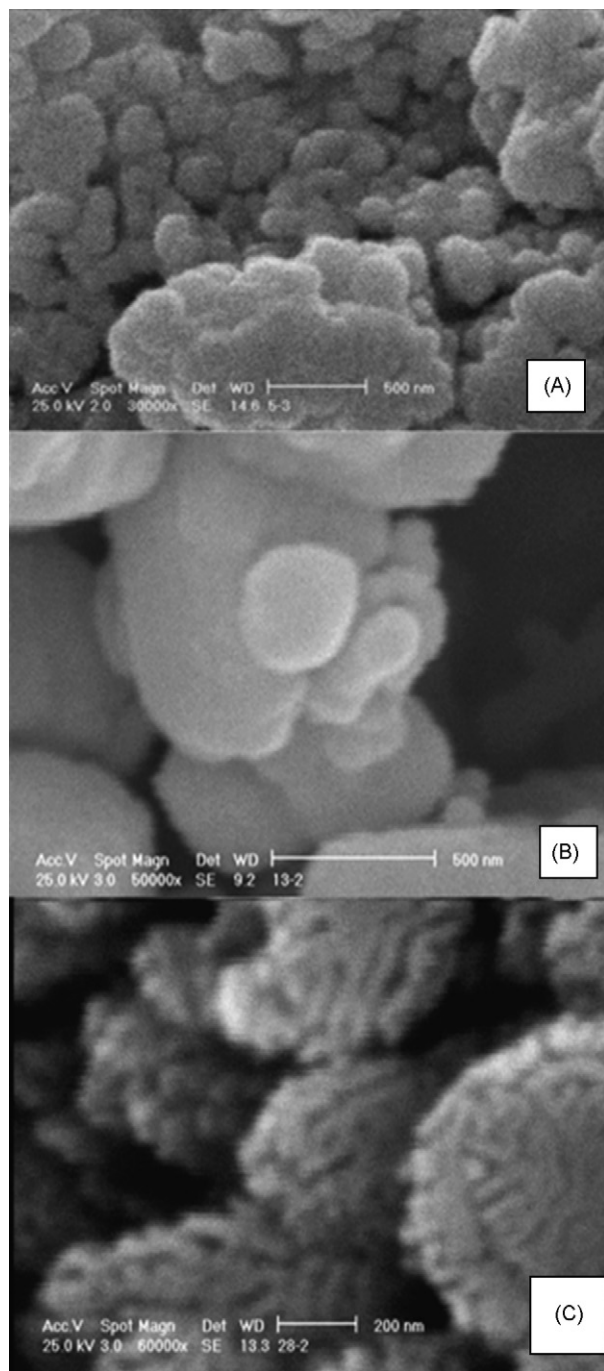


Fig. 7. SEM images of lead oxide samples synthesized at different concentration of PVP: 1 g l⁻¹ (A), 50 g l⁻¹ (B) and 20 g l⁻¹ (C). Other conditions were constant as follows: temperatures of 40 °C, 0.02 M lead nitrate and 0.04 M sodium hydroxide.

The suggested complex can prevent particles from growing. The probable mechanism based on the suggested complex can be expressed as Scheme 1.

For more clarification, The SEM and TEM images of optimum lead oxide powder are shown in Fig. 8.

Fig. 9 shows XRD patterns of the PbO powder synthesized at optimum conditions. In comparison with standard XRD cards, the 2θ peaks observed at these patterns show that the sample includes α -PbO and β -PbO and a very small amount of Pb₃O₄.

Finally, it can be concluded that while the suggested method is used, PbO nanoparticles can be synthesized in nanometer scales (less than 40 nm). In this method, the presence of ultrasonic waves and structure director additives has strong positive effect on the morphology of final product. Prepared lead oxide, under the optimum conditions, is in the moss form and has more porosity.

3.5. Battery making and tests

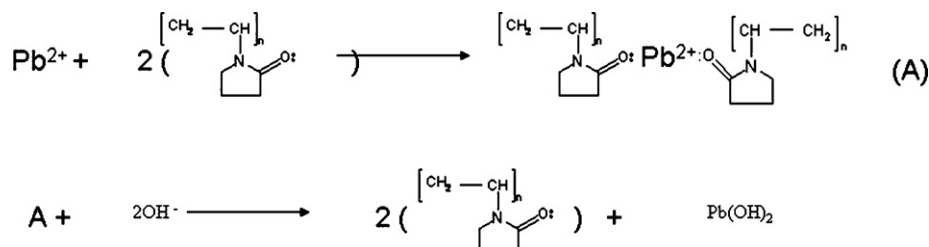
The final lead oxide nanopowder was used as cathode and anode material of lead-acid batteries. Each prepared negative and positive electrode was coupled with commercial counter plate for construction of single unit battery. Each experimental battery was electrochemically made by constant voltage of 2.48 V for 48 h.

At the first step, energy storage ability of negative electrodes was studied. At this stage, eight batteries constructed by the proposed anodes and commercial cathodes. The constructed batteries were discharged by different constant resistances as consumers. Fig. 10 shows the discharge capacity variation versus discharge resistance. As it is seen from Fig. 10a, discharge capacity of battery made of the proposed anode is constant (~ 230 mA h g⁻¹) while discharge resistance density (Ω g⁻¹) is reduced from 260 to 130 Ω g⁻¹. This phenomenon shows that these discharge rates are not large for the battery and the electricity can be produced at this rate. At lower discharge resistances, discharge capacity is slowly decreasing because; at high discharge rates, only the layer of electroactive material close to surface of electrode takes part in discharge reaction and as a result the discharge capacity starts to decrease. Therefore, discharge resistance densities more than 130 Ω g⁻¹ can be used for discharge of the prepared batteries while keeping capacity at maximum level. But with regard to discharge time and discharge current, it is reasonable to select the resistance of 130 Ω g⁻¹ as the discharge resistance so that we can to achieve the highest capacity and high discharge current and low discharge time for the batteries made of the proposed anodes.

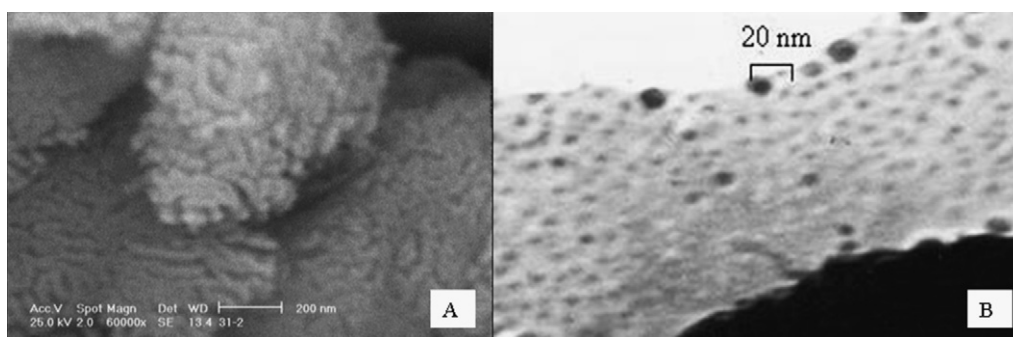
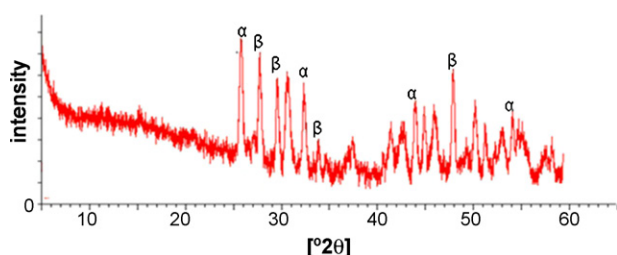
Fig. 10b shows that while the discharge resistance decreases from 231 to 12.5 Ω g⁻¹, the discharge capacity of the batteries made of the proposed cathodes is constant. At lower resistances, discharge current is high and only the layer of electroactive material close to surface of electrode takes part in discharge reaction and then, the discharge capacity starts to decrease. Therefore the discharge resistance of 12.5 Ω g⁻¹ was selected as the optimum resistance for the discharge of batteries made of the proposed cathodes.

While comparing the optimized resistance for the proposed anode and cathode one can understand that the proposed cathode can discharge with higher rates than anode. Probably it is as a result of this fact that the lead dioxide (cathodic material) has more conductivity and can realize the electrical energy at higher rates.

For more investigation into the battery performance, cycle life test was used for the proposed battery made of the proposed anode and cathode and also for the battery made of conventional anode and cathode. At the proposed cycle life test, the sample



Scheme 1. Structure of suggested complex for interaction between PVP and lead ion.

Fig. 8. SEM (A) and TEM (B) images of optimum lead oxide sample. The used conditions were as follows: temperatures of 40 °C, 0.02 M lead nitrate, 0.04 M sodium hydroxide and 20 g l⁻¹ PVP.Fig. 9. XRD patterns for the optimum sample of lead oxide synthesized in the presence of ultrasonic waves and 0.02 M lead nitrate, 0.04 M sodium hydroxide, 20 g l⁻¹ PVP and temperature of 40 °C.

batteries were charged with the constant voltage of 2.48 V for 1 h and discharged with constant resistance density of 12.5 Ω g⁻¹ until the cut-off voltage of 1.75 V. Fig. 11 shows the cycle life behaviors of the proposed battery and conventional battery. As

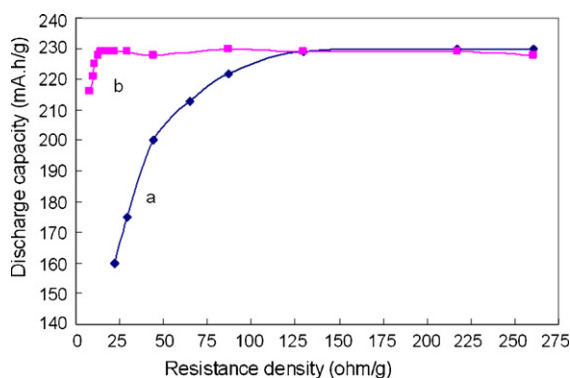
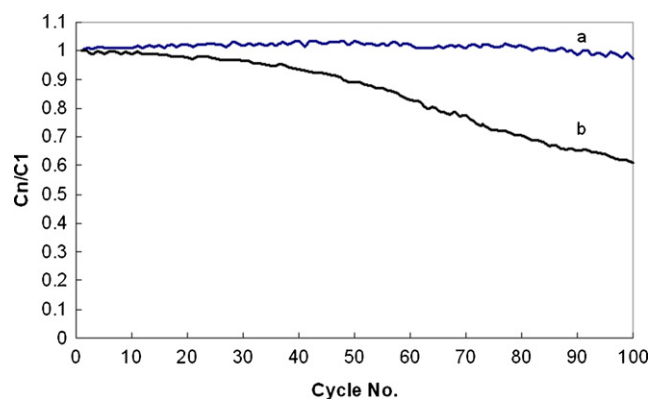


Fig. 10. Variation of discharge capacity with discharge resistance, the battery was constructed by the proposed anode including lead oxide nanoparticle and commercial cathode (a), the battery was constructed by the proposed cathode including lead oxide nanoparticle and commercial anode (b).

it is seen from Fig. 11, during 100 cycles, while the relative discharge capacity of the conventional battery is decreased from 1 to 0.6, a considerable reduction in discharge capacity of the proposed battery is not realized. A comparison between the batteries made of nanostructured lead oxide powder and conventional lead oxide shows that the nanostructured lead oxide keeps the energy storage ability for longer time than the conventional lead oxide. Decreasing discharge capacity during cycle life test can be related to undesirable processes such as tearing and disconnection, passivation and sulfonation. The results of cycle life tests show that the similar undesired processes are not considerable for the paste made of nanostructured lead oxide.

It is believed that in conventional lead-acid batteries, when the particle size of battery leady oxide is more decreased, lower battery performance including lower discharge capacity and shorter

Fig. 11. Variation of relative discharge capacity (relative to first cycle) during the cycle life test for battery made of the proposed nanostructured lead oxide (a) and conventional lead-acid battery (b). C_n is the discharge capacity at the proposed cycle and C_1 is the discharge capacity at cycle 1.

cycle life but is expected. On the contrast, in the batteries made of lead oxide nanoparticles (anode or cathode), this theory is not applicable. The observed excellent performance for lead oxide nanoparticles in lead-acid batteries (as anode or cathode) gives more evidence on the advantages of nanotechnology.

4. Conclusions

Lead oxide can be synthesized in nanoscale in the presence of ultrasonic waves and PVPs as structure directors. The more porous and uniform lead oxide nanopowder can be used as cathode and anode electroactive material in lead-acid batteries. The anodes and cathodes prepared by lead oxide nanoparticles show very excellent discharge capacities and very good cycle life.

Acknowledgements

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References

- [1] F. Nastase, I. Stamatina, C. Nastase, D. Mihaiescu, *Prog. Solid State Chem.* 34 (2006) 191.
- [2] S.H. Yoon, J.S. Kim, Y.S. Kim, *Curr. Appl. Phys.* 6S1 (2006) e154.
- [3] Y.Q. Huang, L. Meidong, Z. Yike, L. Churong, X. Donglin, L. Shaobo, *Mater. Sci. Eng. B* 86 (2001) 232.
- [4] Z. Wang, S.K. Saxena, *Solid State Commun.* 118 (2001) 75.
- [5] H. Gong, J.Q. Hu, J.H. Wang, C.H. Ong, F.R. Zhu, *Sens. Actuators B* 115 (2006) 247.
- [6] H. Bode, *Lead-acid Batteries*, Wiley, New York, 1977.
- [7] N.K. Bullock, R.A. Peterson, US Patent 5,149,606 (1992).
- [8] W.H. Kao, N.K. Bullock, R.A. Peterson, US Patent 5,302,476 (1994).
- [9] M.L. Soria, J. Valeciano, A. Ojeda, *J. Power Sources* 136 (2004) 376.
- [10] D. Pavlov, G. Petkova, M. Dimitrov, M. Shiomi, M. Tsubota, J. Power Sources 87 (2000) 39.
- [11] C.-H. Yeh, C.-C. Wan, J.-S. Chen, *J. Power Sources* 101 (2001) 219.
- [12] Z. Shi, Y.-H. Zhou, C.-S. Cha, *J. Power Sources* 70 (1998) 205.
- [13] R. De Marco, A. Lowe, M. Sercombe, P. Singh, *Electrochim. Acta* (2005).
- [14] M. Shiota, T. Kameda, K. Matsui, N. Hirai, T. Tanaka, *J. Power Sources* 144 (2005) 358.
- [15] J.-S. Chen, *J. Power Sources* 90 (2000) 125.
- [16] P.K. Shen, X.L. Wei, *Electrochim. Acta* 48 (2003) 1743.
- [17] D. Devilliers, M.T. Dinh Thi, E. Mahé, V. Dauriac, N. Lequeux, *J. Electroanal. Chem.* 573 (2004) 227.
- [18] N. Vatisas, S. Cristofaro, *Electrochem. Commun.* 2 (2000) 334.
- [19] S. Ghasemi, H. Karami, M.F. Mousavi, M. Shamsipur, *Electrochem. Commun.* 7 (2005) 1257.
- [20] S. Ghasemi, M.F. Mousavi, H. Karami, M. Shamsipur, S.H. Kazemi, *Electrochimica Acta* 52 (2006) 1596.
- [21] M. Cruz, L. Hernán, J. Morales, L. Sánchez, *J. Power Sources* 108 (2002) 35.
- [22] K. Konstantinov, S.H. Ng, J.Z. Wang, G.X. Wang, D. Wxler, H.K. Liu, *J. Power Sources* 159 (2007) 241.
- [23] G. Henshaw, I.P. Parkin, G. Shaw, *J. Chem. Soc., Dalton Trans.* (1997) 231.
- [24] V. Dusastre, B. Omar, I.P. Parkin, G. Shaw, *J. Chem. Soc., Dalton Trans.* (1997) 3505.
- [25] K.S. Suslick, M. Fang, T. Hyeon, *J. Am. Chem. Soc.* 118 (1996) 11960.
- [26] T. Hyeon, M. Fang, K.S. Suslick, *J. Am. Chem. Soc.* 118 (1996) 5492.
- [27] K.S. Suslick, *MRS Bull.* 20 (1995) 29.
- [28] O. Rozenfeld, Y. Koltypin, H. Bomnolker, S. Margel, A. Gedanken, *Langmuir* 10 (1994) 3919.
- [29] K.S. Suslick, S.B. Choe, A.A. Cickowlas, M.W. Grinstaff, *Nature* 353 (1991) 414.
- [30] K. Okitso, Y. Mizukoshi, H. Bondow, Y. Macda, T. Yamamoto, Y. Nagata, *Ultrason. Sonochem.* 3 (1996) S249.
- [31] J.H. Zhang, X.G. Yang, D.W. Wang, Y. Xie, Y.T. Qian, *Inorg. Chem. Commun.* 2 (1999) 447.
- [32] J.C. Miller, J.N. Miller, *Statistics for Analytical Chemistry*, 2nd ed., Chichester, Horwood, 1988.
- [33] M. Cao, C. Hu, G. Peng, Y. Qi, E. Wang, *J. Am. Chem. Soc.* 125 (2003) 4982.
- [34] Z. Zhang, B. Zhao, L. Hu, *J. Solid State Chem.* 121 (1996) 105.